Thermal behavior and kinetics of bio-ferment residue/coal blends during co-pyrolysis

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A B S T R A C T

In this work, the thermal behavior and kinetics of bio-ferment residue (BR) and coal blends during co-pyrolysis were investigated using TG-FTIR and kinetic analysis. The co-pyrolysis of BR and coal occurred in three major stages. The BR/coal blends lost most of their weight during the devolatilization stage. The kinetics of the BR/coal blends in this stage implied that the activation energy was lower than that of BR and coal below a certain BR blending ratio. The BR/coal blends started to decompose at approximately 45 °C, releasing ammonia followed by alkanes, carbon dioxide, methane and carbon monoxide. The total yield of gaseous products (primarily ammonia, alkanes and carbon dioxide) increased with increasing BR blending ratio. Moreover, interactions most likely occurred between the BR and the coal during co-pyrolysis.

1. Introduction

In recent years, the generation of hazardous waste in China has continuously increased. The disposal facilities for hazardous waste are far from meeting the demands from growing waste productions. The construction of new disposal facilities is a long-term and high-cost endeavor. Thus, the employment of existing facilities for hazardous waste co-disposal can be a partial solution in the near-term. The method of co-disposal depends on the properties of the specific hazardous wastes.

Bio-ferment residual (BR) is a typical type of pharmaceutical waste that contains large amounts of toxic organics. BR is identified as hazardous waste (HW02 Toxicity) [1] by the Ministry of Environmental Protection of China. BR is produced through biological fermentation and is primarily composed of cell debris. The biomass characteristics of BR make it suitable for co-disposal in high temperature boilers. However, researches on this subject [2] mainly focused on co-combustion. In this work, we focus on co-pyrolysis as a method for co-disposal.

Aboulkas et al. [3,4] studied co-processing of olive residue with polypropylene and co-pyrolysis of oil shale and poly (ethylene terephthalate) using a thermogravimetric (TG) analyzer in an inert atmosphere. The pyrolysis of the mixtures was compared with that of the individual components. The differences between the experimental and calculated TG curves were considered as a measurement of interactions occurring in co-pyrolysis. Zhou et al. [5] studied co-pyrolysis of coal and three kinds of plastics through TG and kinetic analysis. Synergistic effect between mixtures was found to mainly occur in the high temperature during pyrolysis. Çepelioğullar and Pütün [6] also employed TG and kinetic analysis to study co-pyrolysis of biomass and plastic. Significant changes in the thermal and kinetic behaviors were considered as a result of co-pyrolysis. Fernández-Berridi et al. [7] used TG and Fourier Transform Infrared spectroscopy (FTIR) analysis in tires for quantitative determination of elastomer blends. Ren et al. [8] studied co-pyrolysis behavior of municipal solid waste (MSW) and biomass using TG-FTIR analysis to investigate pyrolysis characteristic and pollutant emission performance of mixture at different mass proportions. The well-established technique of TG and FTIR analysis has been applied widely in co-disposal investigation. TG-FTIR analysis of bio-ferment residue has been carried out [9] to study its co-combustion in a MSW incineration plant. It was found that the thermal behavior of bio-ferment residue was similar in pyrolysis and combustion conditions at low temperature. Although pyrolysis has been previously investigated for the BR, there are no reported studies involving BR and coal co-pyrolysis.

In view of this, TG-FTIR and kinetic analysis were employed to study the thermal behavior and kinetics of BR/coal blends during co-pyrolysis.

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2. Materials and methods

2.1. Samples

The proximate and ultimate analysis of BR and coal are given in Table 1. The proximate analysis was based on the Coal Industry Analysis Method (GB/T 212-2008). The ultimate analysis was performed using an elemental analyzer (1ECO-CMNS932). The fluorine and the chlorine were measured using the combustion hydrolysis method followed by an ion chromatography (IC 792) analysis. The calorific value was measured according to the Determination of Calorific Value of Coal (GB/T 213-2008).

The results of ultimate and proximate analysis for BR and coal are compared in Table 1. It can be observed that BR has much higher volatile content, H/C ratio and oxygen content than coal. It is most likely that BR and coal have different composition of volatile. BR and coal have similar sulfur and nitrogen contents. Their contents of fluorine and chlorine are very low.

2.2. Experiments

A Mettler Toledo TGA/SDTA851e thermo analyzer coupled with a Nicolet Nexus 670 spectrometer was used for TG-FTIR analysis. According to Aboyade's research [10], during slow pressurized pyrolysis of coal and biomass, the volatile products were mostly influenced by mix ratio rather than temperature or pressure. Thus, BR and coal blends at different mix ratio (80%, 60%, 40% and 20% by weight) were studied. The coal was on as-received basis, while the BR was on air-dry basis. In each experiment, approximately 10 mg of sample was used. A constant flow of nitrogen (50 ml/min) was introduced into the thermo analyzer furnace. Slow heating rate is good for separating pyrolysis stages [11]. Thus, the sample was heated at slow heating rates of 10, 30 and 50 °C/min from 25 to 1000 °C. Temperature was then held at 1000 °C for 20 min. At the same time, the gaseous products were immediately swept into the FTIR gas cell through a pipe. The pipe was kept at 180 °C [12], so that the heavy liquid (tar) present in the gas cell was in the form of an aerosol. The FTIR spectra had a wavenumber range between 400 and 4000 cm^{-1}.

2.3. Kinetic method

Based on the TG data, kinetic parameters were calculated for BR and coal co-pyrolysis. Pyrolysis could be considered as a volatile release process. Thus, the activation energy fit the following equation:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{1}$$

Here, α is the conversion degree for individual pyrolysis stage; A is the Arrhenius pre-exponential factor; β is the heating rate; E is the activation energy for individual pyrolysis stage; R is the gas constant; T is the pyrolysis temperature; $f(\alpha)$ is the pyrolysis function.

Coats–Redfern [13] method was used for thermal dynamic analysis. The equation is as follow:

If $n \neq 1$,

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

If $n = 1$,

$$\ln\left[\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

Here, n is the reaction order for individual pyrolysis stage.

3. Results and discussion

3.1. Pyrolysis behaviors of coal

Fig. 1 gives the TG and DTG (differential thermogravimetric) profiles for coal pyrolysis at three heating rates (10, 30 and 50 °C/min). The weight (TG) and weight loss rate (DTG) of coal are plotted as a function of temperature. The heating rate only influences the reaction rate (i.e. weight loss rate), but has a negligible effect on the pattern of coal pyrolysis. Thus, the pyrolysis at one of the three heating rates (30 °C/min) was analyzed.

The coal pyrolysis occurs in two distinct stages. The first stage occurs in a temperature range of 25–170 °C and is caused by the moisture evaporation. The second stage occurs above 300 °C and is mainly a devolatilization stage. The volatiles evolve at a high rate below 545 °C. The devolatilization rate (i.e. weight loss rate) reaches maximum at approximate 475 °C and decreases significantly when the temperature rises above 600 °C. At the high temperature above 600 °C, further decomposition of volatiles take place and ring condensation and re-solidification occur [14]. The TG results show that the solid residual occupies 65.00 wt.% of the original sample weight when the temperature first reaches 1000 °C.

Fig. 1 also gives the FTIR spectrum at the maximum devolatilization rate in coal pyrolysis. The absorption bands for alkyl groups (3000–2850 cm^{-1}), carbon monoxide (2270–1980 cm^{-1}), carbon dioxide (2400–2230 cm^{-1}), methane (3200–2800 cm^{-1}) and water (4000–3400, 2100–1200, 700–400 cm^{-1}) are obviously observed.

3.2. Co-pyrolysis behaviors of BR and coal

Fig. 2 gives the TG/DTG profiles for pyrolysis of BR, coal and BR/coal blends at a heating rate of 30 °C/min. The TG curves are plotted as a function of time rather than temperature so that the change in weight of the sample that occurs when the temperature reaches as stable 1000 °C can be shown. The DTG curves are presented as a function of temperature.

The TG/DTG analysis shows that there are three distinct stages of co-pyrolysis for BR and coal blends. The first stage is the moisture evaporation stage and the second stage is the devolatilization stage. Both stages are similar to those of coal. The third stage in pyrolysis occurs above 600 °C and is mainly attributed to ring

Table 1
Ultimate and proximate analysis of samples [2] (air dry basis).

	M wt.%	A wt.%	V wt.%	Fc wt.%	HHV MJ/kg	C wt.%	H wt.%	O wt.%	N wt.%	St wt.%	F wt.%	Cl wt.%
Coal	6.01	20.61	29.25	44.13	23.39	55.6	3.16	10.81	1.08	0.43	<0.05	<0.05
BR	9.71	14.21	67.29	8.79	18.64	40.12	8.84	25.52	1.19	0.41	<0.05	<0.05

M, moisture; A, ash; V, volatiles; Fc, fixed carbon; HHV, higher heating value on dry basis; C, carbon; H, hydrogen; O, oxygen; N, nitrogen; St, total sulfur; F, fluorine; Cl, chlorine
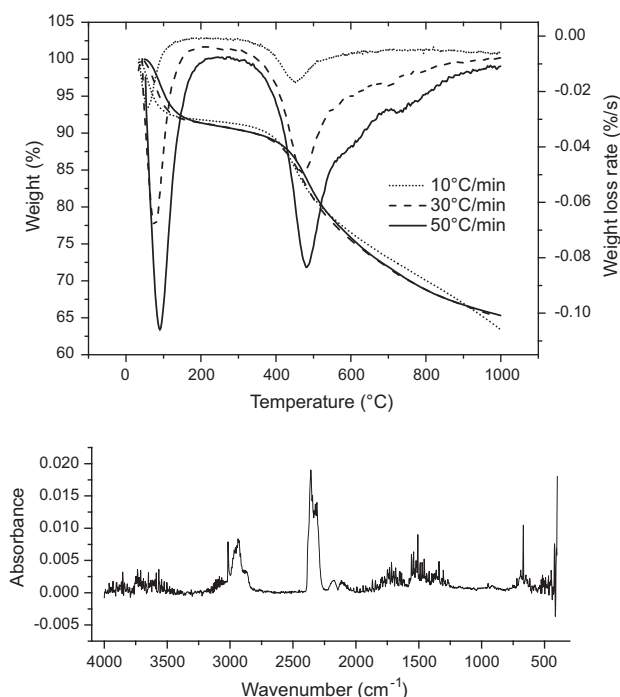
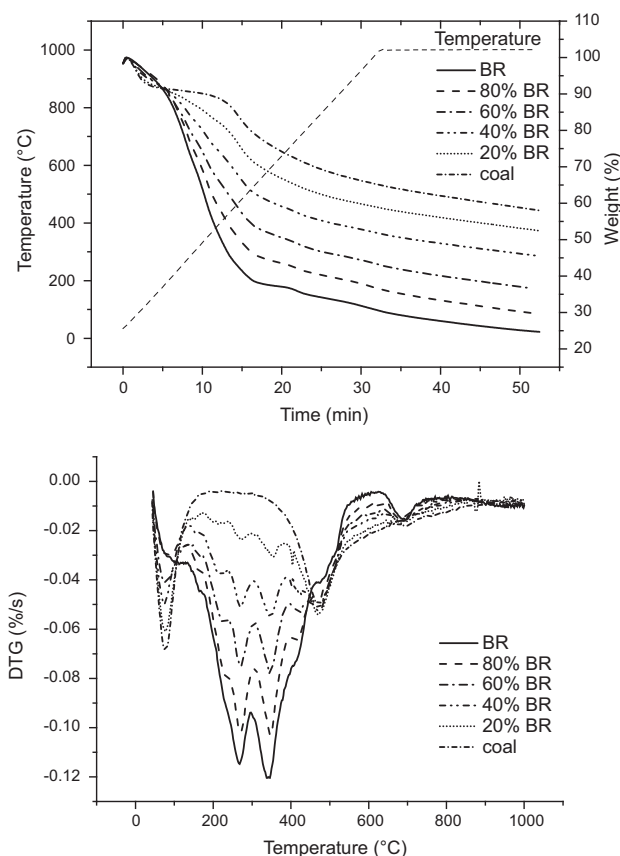**Fig. 1.** TG, DTG and FTIR analysis of coal pyrolysis.

Fig. 2. TG and DTG analysis of BR/coal blends during co-pyrolysis (30 °C/min).

condensation and re-solidification, which overlap with the slow devolatilization stage in coal pyrolysis.

Marked differences in the TG/DTG curves can be observed between the pyrolysis of the blends and the pyrolysis of the individual components. The devolatilization stage of the BR/coal blends occurs at a much lower temperature than that of coal. The volatile content is relatively low in coal, but it increases with increasing BR blending ratio. The general devolatilization rate tends to increase with the BR blending ratio. These differences deduced from TG/DTG results are supported by the FTIR analysis described below.

The initial evolution temperature, the maximum reaction rate (moisture evaporation stage not included) and the reaction temperature are summarized in Table 2. The initial evolution temperature for pyrolysis of the blends is reduced to ca (circa) 45 °C. Moreover, the temperature at the maximum reaction rate shifts from ca 470 °C to ca 345 °C when the BR blending ratio reaches a value between 20% and 40%. As the temperature rises to 600 °C, the devolatilization process slows down. The Tve is defined as the temperature at which the release of volatiles is almost complete. It is determined by the turning point at a weight loss rate of 0.0075%/s, when rapid weight loss no longer occurs. The Tvb and Tve of the blends are much lower than those of coal due to the volatile content of the BR. The yield of solid residual decreases significantly with an increase in the BR blending ratio. In contrast, the weight loss (i.e. the gas yield) increases dramatically with increasing BR blending ratio, as shown in Table 2. The yields of product in gaseous and solid phase are basically linear to the BR blending ratio. Interactions between the coal and the BR cannot be inferred by the total yield of gaseous products.

3.3. Kinetic analysis

Activation energy, pre-exponential factor and reaction order are evaluated based on the TG data from pyrolysis at a heating rate of 30 °C/min. Table 3 gives the kinetic parameters for the fast devolatilization stage.

Based on the kinetic parameters listed in Table 3, the reaction order of the coal in the fast devolatilization stage is a very low value of 1.00, while the reaction order of the blends generally increases with the BR blending ratio. This value becomes larger than that of BR as the percentage of BR reaches 60%. Because BR starts to decompose at a much lower temperature than coal, the energy barrier for the volatiles in BR to evolve are lower than for the volatiles in coal. The activation energy for BR is supposed to be lower than for coal. However, as shown in Table 3, BR has higher activation energy than coal in the devolatilization stage. This is because the volatile percentage released from BR is much larger than for coal. It is not surprising that when the BR ratio is lower than 50%, the mixture exhibits lower activation energy than coal. The activation energy of the mixture increases with the BR blending ratio because the BR has higher activation energy than coal in the devolatilization stage.

3.4. Co-pyrolysis products of BR and coal

Integration over a specific wavenumber of the FTIR spectra provides the concentrations of species as a function of time/temperature. The evolution curves obtained for gaseous products by FTIR spectroscopy of the pyrolysis of the blends and the individual components at the heating rate of 30 °C/min are overlaid in Fig. 3. All of the initial sample weights are adjusted to 10 mg. The absorbance is plotted as a function of time including the 20 min that the temperature is held at 1000 °C. Various species, such as alkanes, CO, CO_2, CH_4 and NH_3, are identified. From Fig. 3, essential distinctions can be observed in the evolution patterns between the different pyrolysis products.

Alkanes (alkyl group) are usually contained in organic matter. Coal releases alkanes as a single peak from 363 to 644 °C, while the alkanes in BR/coal blends start to evolve at much lower

Table 2
Co-pyrolysis characteristics of BR and coal.

Sample	Tvb °C	Tve °C	Rm %/s	Tm °C	Gas yield (calculated by difference) wt.%	Solid yield wt.%
BR	45.25	566.89	0.120	341.81	75.32	24.68
80% BR	45.30	740.95	0.103	346.10	70.40	29.60
60% BR	45.38	792.57	0.078	344.07	63.63	36.37
40% BR	45.31	834.10	0.055	347.48	54.50	45.50
20% BR	43.42	882.18	0.054	469.61	47.55	52.45
Coal	250.59	975.64	0.050	469.23	41.97	58.03

Tvb, the temperature volatile starts to evolve; Tve, the temperature volatile releasing is almost completed; Rm, the maximum reaction rate; Tm, the temperature at the maximum reaction rate.

Table 3
Comparison of the kinetic parameters (170–600 °C).

	E (kJ/mol)	A (min^{-1})	R	n
BR	39.81	8.47E+02	0.978	1.4
80% BR	38.18	5.39E+02	0.974	1.45
60% BR	36.22	2.94E+02	0.969	1.45
40% BR	34.04	1.42E+02	0.967	1.38
20% BR	30.66	3.82E+01	0.97	1.1
Coal	35.05	4.67E+01	0.969	1

E, activation energy; A, pre-exponential factor; R, linear correlation coefficient; n, reaction order.

temperatures. Their release rate increases with the BR blending ratio. As the temperature rises above 600 °C, the evolution of alkanes decreases for BR, coal, and BR/coal blends. This is consistent with the TG analysis for co-pyrolysis. For the pyrolysis of BR, coal and their blends, the evolution of CO mainly occurs at higher temperatures than the evolution of alkanes. The release of carbon monoxide is related to the ring condensation and re-solidification at high temperatures. It is not surprising that carbon dioxide, the precursors of which are very complicated for coal and BR, shows no clear relationship between release rate and BR blending ratio. Methane generally evolves as a single peak for coal, while BR/coal blends have an additional shoulder for methane at the lower temperature side of the peak. The methane shoulder becomes larger with increasing BR blending ratio. As the temperature rises above 750 °C, the release of methane decreases for BR, coal, and their blends. Although BR and coal have similar N content, they have different nitrogen evolution behaviors. Coal exhibits almost no ammonia peak, while BR has a distinct peak for ammonia. This is because BR and coal have different functional forms of nitrogen, which determines the migration characteristics of N during pyrolysis, i.e., the reaction mechanisms and the products [15,16]. The BR/coal blends start to release ammonia at temperatures even lower than for alkanes. The early release of ammonia is consistent with the previous TG observation of the initial evolution temperature.

The yield of each species is in proportion to the area under the evolution curve in Fig. 3. In Fig. 4, the integration of absorbance in the evolution curve for BR, coal and their blends is presented as the ratio to coal evolution. The integration for each species is plotted as a function of the BR percentage.

Fig. 4 shows that BR exhibits slightly lower yields of CO and CH$_4$ than coal, but obviously larger yields of NH$_3$, alkanes and CO$_2$. For the mixture of BR and coal, CO and CH$_4$ show yields decrease with increasing BR blending ratio, while NH$_3$, alkanes and CO$_2$ yields increase. To estimate the interaction between BR and coal during co-pyrolysis, the experimental product yields are compared to the theoretical yields calculated as the algebraic sum of the experimental yields of the individual components. In theory, the larger the difference between the experimental and theoretical yields,
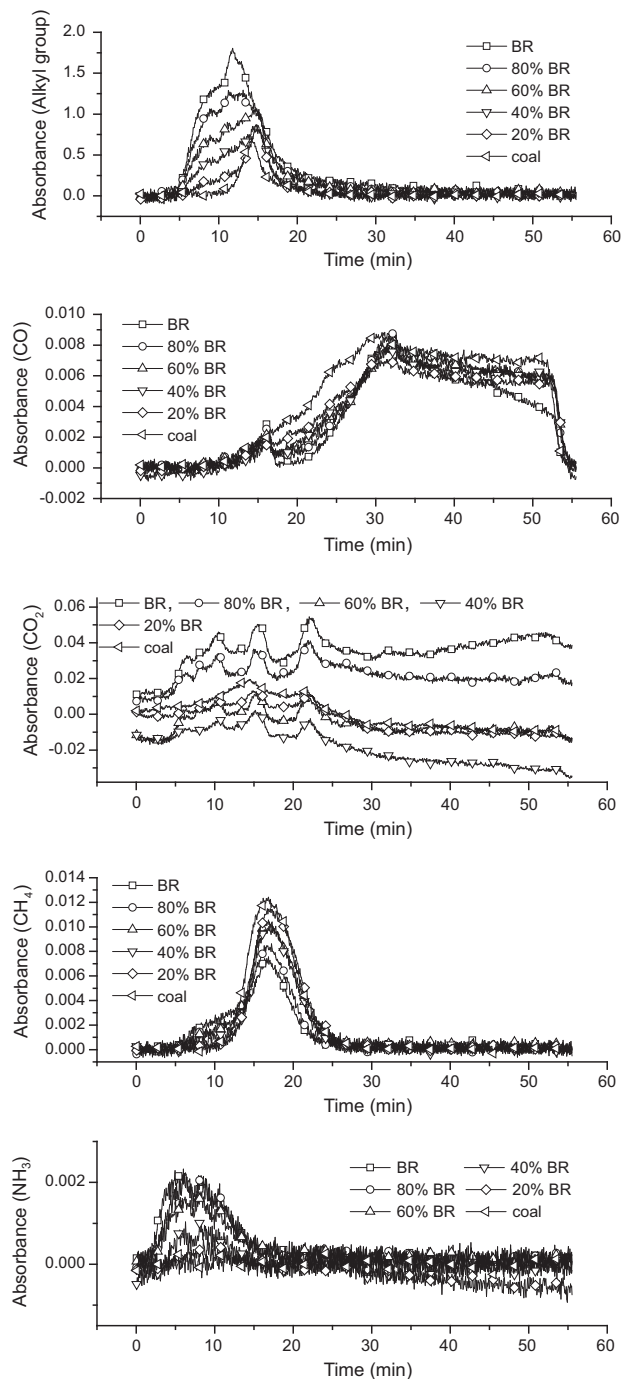
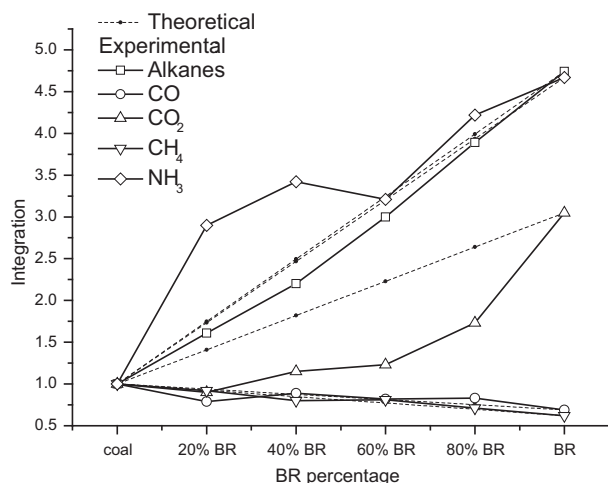**Fig. 3.** The evolution curve for pyrolysis products of BR, coal and their blends.

Fig. 4. Comparison of pyrolysis product yields for BR, coal and their blends.

the more obvious the interaction will be. For alkanes, CH_4 and CO, the experimental yields are close to the theoretical yields, i.e., these three products have a linear relationship with the BR blending ratio. However, the experimental yields are greater than the theoretical yields for NH_3 and lower than the theoretical yields for CO_2. The marked differences between the experimental and theoretical yields for NH_3 and CO_2 confirm the interactions between BR and coal during co-pyrolysis.

4. Conclusions

Through TG-FTIR and kinetic analysis of BR and coal during co-pyrolysis, the following results were found. There were three major stages in BR/coal co-pyrolysis. Most of the weight of BR/coal blends was lost during the devolatilization stage. In this stage, the activation energy increased with the BR blending ratio. It was worth noting that the activation energy of blends could stay lower than that of BR and coal below a certain BR blending ratio. The devolatilization of BR/coal blends started around 45 °C (much lower than for coal) releasing ammonia followed by alkanes, carbon dioxide, methane and carbon monoxide. The yield of ammonia, alkanes and carbon dioxide increased significantly with increasing BR blending ratio, while the yield of methane and carbon monoxide decreased slightly. The total yield of gaseous product calculated by difference increased with increasing BR blending ratio. By comparing the experimental yields with the theoretical yields, it was found that interactions most likely occurred between the BR and the coal during co-pyrolysis.

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